The Gas Chromatographic Determination of Paraquat in Water

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INTRODUCTION

Paraquat [1,1'-dimethyl-4,4'-bipyridinium dichloride (I) or bis(methyl sulfate)] and diquat [6,7-dihydrodipyrido(1,2-a:2',1'-c)-pyrazidiinium dibromide (II)] are bipyridinium herbicides registered for a variety of uses on both field and orchard crops (1). They can enter waterways indirectly through irrigation runoff. They have also been used successfully for the control of various aquatic weeds (2), and could directly contaminate both irrigation and domestic water in this way.

While paraquat is dissipated in water rather rapidly, probably through photolysis and adsorption, a finite level still may remain for some time. For example, while reservoirs treated at 1 to 3 ppm with paraquat showed a 73% loss of herbicide in 1 day, levels of 80 to 300 ppb remained after 12 days (3).

Analytical methods for paraquat residues in water include colorimetric (4) and bioassay (5) techniques. The colorimetric method involves the concentration and cleanup of samples by cation exchange chromatography followed by reduction with sodium dithionite and comparison of the absorbance at 600 nm with that from standards. With a 200 g sample, recoveries of 70% and a limit of detectability of 0.01 ppm are possible (4). The major drawbacks to the existing method are the time-consuming ion-exchange step, the lack of specificity imposed by colorimetric detection, and reported non-adherence to Beer's Law by bipyridinium compounds (6).

The purpose of this research was to devise a gas chromatographic (GLC) analytical method for paraquat in which both the resolution and specific detection could be accomplished in one step. Paraquat is a nonvolatile salt with a high, indefinite decomposition point. Preliminary work in our laboratory indicated that it could be thermally dealkylated to 4,4'-bipyridyl above 300°C in the injection port of a gas chromatograph, hydrogenated to yield a mixture of bipiperidine compounds in a pre-column apparatus similar to the Beroza carbon-skeleton determinator (7), or hydrogenated in aqueous or methanolic solution with Adams Catalyst. The latter method, found to be simple, inexpensive, and reproducible, involved complete hydrogenation of paraquat to 1,1'-dimethyl-4,4'-bipiperidine (III) in aqueous solution, extraction

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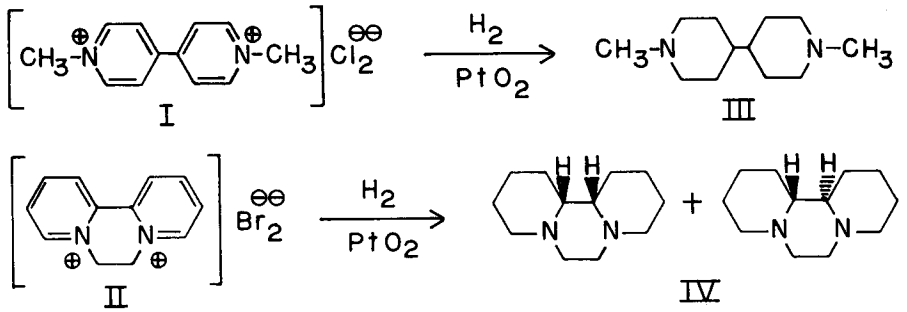
into organic solvent, and analysis by flame-ionization GLC.



MATERIALS AND METHODS

Chemicals. All solvents were reagent grade. Platinum oxide (Adams Catalyst) was purchased in 1.0 g packages from Matheson, Coleman & Bell, Inc. Paraquat dichloride and diquat dibromide were manufacturer's analytical standards.

1,1'-Dimethyl-4,4'-bipiperidine was prepared by bubbling hydrogen into a mixture of 1.0 g of paraquat dichloride and 50 mg of PtO_2 in 30 ml of methanol for 18 hrs at room temperature. The methanol was evaporated to about 5 ml, 25 ml of 1 N NaOH solution was added, and the mixture was extracted with hexane. Evaporation of the hexane provided 0.41 g (85% yield) of a white solid, m.p. 52-53°C (lit. 57-59°C) (8). The product was characterized by infrared (KBr) absorption at 3.38, 3.55 and 7.78 μ, nmr absorption (deuteriochloroform, TMS internal standard) at 2.27 ppm (CH_3) and 1.0-3.0 ppm (CH_2), and mass spectral parent peak at m/e 196. Elemental analysis indicated a monohydrate (calc. for $C_{12}H_{26}N_2O$: C,67.20; H,12.25; N,13.08; found: C,67.66; H,12.42; N,12.33).

Hydrogenation of diquat dibromide under the same conditions, followed by GLC, yielded two products, presumably the cis and trans isomers of perhydro dipyrido[1,2-a:2',1'-c]pyrazine (IV). The isomers were liquids with identical mass spectra (parent peak m/e 194) but slightly different nmr and ir spectra. The m.p. of their picrates, 258-9°C dec. and 262-3°C dec., agreed generally with that reported for the unresolved mixture, m.p. 248-52°C dec.(9).

Gas Chromatography. A Varian-Aerograph Model 1700 gas chromatograph equipped with a flame ionization detector and a 6 foot x 1/8 inch (od) glass column packed with 10% Triton X-100 plus 1% KOH on 70/80 AW, DMCS treated Chromosorb G was used. Oven temperature, 150°C; injection port, 200°C; detector, 210°C; carrier gas (nitrogen) at 30-40 ml/min. 1,1'-Dimethyl-4,4'-bipiperidine had a retention time of 8 minutes.

Determination. A 100 ml water sample was placed in a 2-neck, 100 ml round bottom flask equipped with a Teflon stir bar, a dry-

ice trap in the vertical neck, and an adapter to hold a disposable glass pipette drawn to a capillary point in the side neck. Concentrated H_2SO_4 (3 ml) and 25 mg of PtO_2 were added and cylinder hydrogen was bubbled through the capillary tube with stirring for 1 hour. The contents of the flask and trap were rinsed into a 250 ml separatory funnel with methylene chloride, 11 ml of 50% NaOH solution was added, and the aqueous layer was extracted with three 50 ml portions of methylene chloride. The extracts were combined with 4 ml of 1 N HCl and evaporated on a rotary evaporator (50-55°C bath) until only the aqueous portion remained. This was transferred with a 1 ml, 0.01 N HCl rinse into a 15 ml screw-cap test tube, 0.5 ml of 50% NaOH solution and 1.00 ml of CS_2 were added and the mixture was shaken briefly. Aliquots of the CS_2 (lower) phase (1-10 µl) were injected into the gas chromatograph, and the response was compared to values from a standard curve.

RESULTS AND DISCUSSION

Various parameters were examined in order to obtain the highest possible recovery. A number of GLC stationary phases were tried; the only one which gave non-tailing peaks and minimized column loss was a Triton X-100/KOH combination. While KOH-treated columns have been recommended for amine analysis (10), their use was limited by the appearance of "ghost peaks" (11), and care must be taken to avoid injection of water. Carbon disulfide was chosen as the solvent due to its minimal flame-ionization response and water immiscibility. 1,1'-Dimethyl-4,4'-bipiperidine has appreciable volatility, and an acidic "keeper" must be added to prevent loss during the evaporation of the methylene chloride extract.

The conditions of the hydrogenation step were studied intensively. Analysis of aliquots of a 10 ppm paraquat sample withdrawn at intervals gave the curve shown in Figure 1. The reaction was complete in about 60 minutes. Yields were fairly constant over a pH range of 1 to 9. While synthesizing gram quantities of 1,1'-dimethyl-4,4'-bipiperidine, it was noted that yield and purity depended upon the batch of PtO_2 used; care should be taken to use one particular bottle of catalyst throughout any set of analyses.

Sub-samples (100 ml) from a 22 liter sample of American River water taken at Discovery Park, Sacramento, California in February, 1972 were fortified with 0.1, 0.5 and 1.0 ppm of paraquat and analyzed to give the standard curve represented by Figure 2. Peak heights and peak areas gave similar results. Comparison of peak heights corrected for the change in molecular weight (observed X 186/196 = corrected) with a 10 ng/µl standard of 1,1'-dimethyl-4,4'-bipiperidine in CS_2 gave recoveries of 43, 37, 36 and 38% for 0.1, 0.5, 1.0 and 5.0 ppm. Fortification of a water sample with 1,1'-dimethyl-4,4'-bipiperidine at a level equivalent to 0.1 ppm paraquat provided a 90% recovery; the low recoveries must result from the hydrogenation step, but no explanation was found.

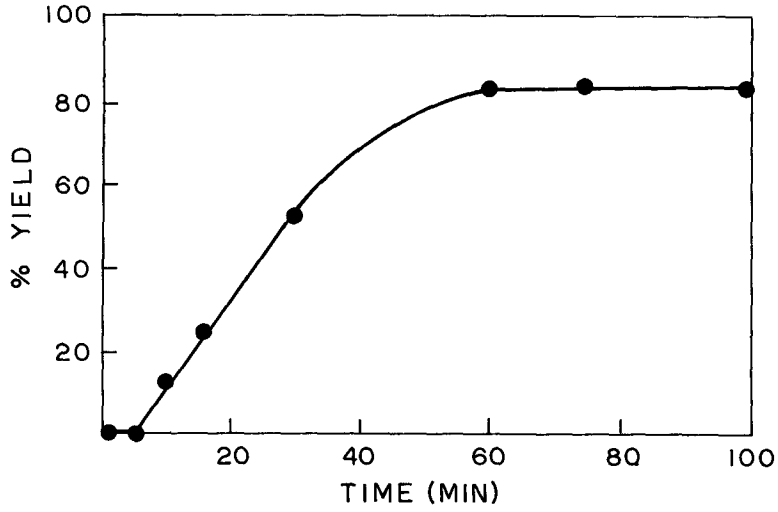


Figure 1
Rate of Hydrogenation of Paraquat to III.

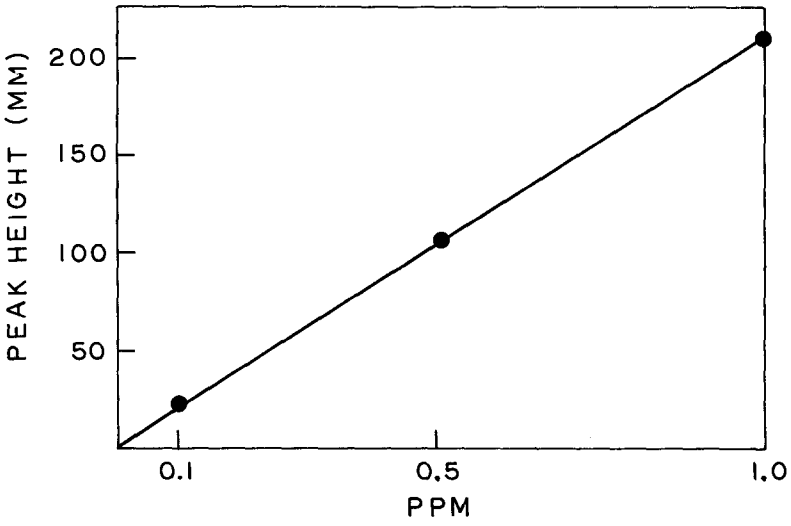


Figure 2
Standard Curve for Paraquat.

By fortifying blank samples with paraquat in amounts near the expected residue level and plotting a standard curve directly, one can avoid the macro-scale synthesis of 1,1'-dimethyl-4,4'-bipiperidine for standard solutions and automatically include corrections for recoveries and molecular weight changes. In this instance,

neither deionized water nor river water provided any interferences (Figure 3).

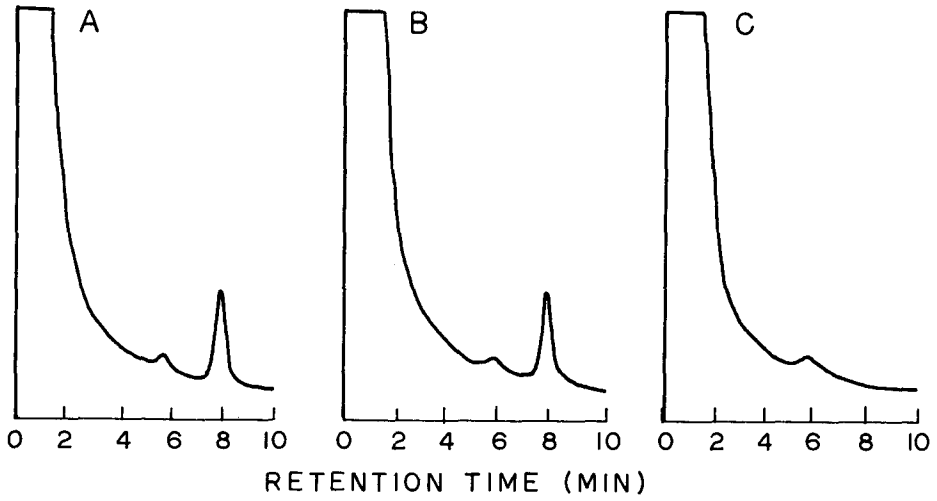


Figure 3
Gas Chromatograms of (A) 0.1 ppm paraquat in deionized water; (B) 0.1 ppm paraquat in river water; (C) river water control.

The new paraquat procedure was applied to diquat in water, resulting in a chromatogram shown in Figure 4A. The isomer appearing at 8 minutes on this column co-chromatographed with 1,1'-dimethyl-4,4'-bipiperidine as shown in Figure 4B where equal amounts of paraquat and diquat were analyzed together.

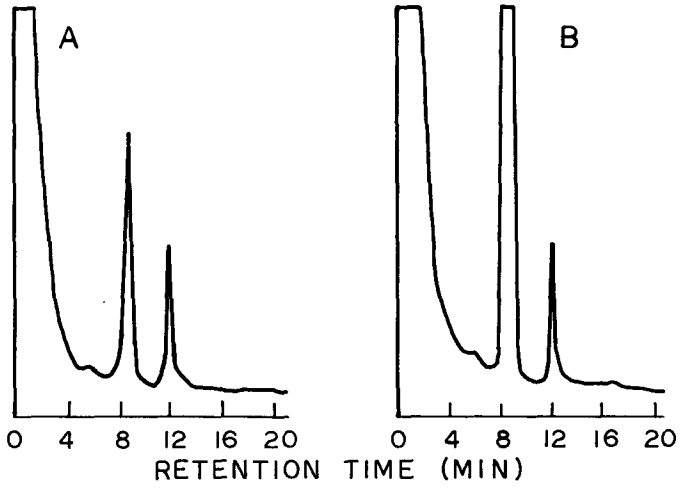


Figure 4
Gas Chromatograpm of (A) 1 ppm diquat in river water; (B) 1 ppm diquat plus 1 ppm paraquat in river water.

Attempts to apply this procedure to crop materials were unsuccessful. Fortified potato samples were digested according to Pack (4) and further cleaned up by isobutanol and methylene chloride extraction. Hydrogenation of the resulting aqueous solution gave no recovery of paraquat at 1 ppm. The failure of the hydrogenation remains unexplained.

The procedure outlined here has a limit of detectability of less than 0.1 ppm but recoveries of only 36-43% at 0.1 to 1.0 ppm. The limit of detectability may be extended by preconcentrating a larger water sample by evaporation or by hydrogenating a larger water sample. While the recoveries were low, they were constant and reproducible. The analysis requires less than 1 hr per sample and a minimum of equipment. This method also may be used for qualitative confirmation of paraquat or diquat residues.

ACKNOWLEDGEMENTS

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REFERENCES

1. U.S.D.A., Summary of Registered Agricultural Pesticide Chemical Uses, 3rd Ed., Vol. 1, 1968.
2. H.H. FUNDERBURK, in "Degradation of Herbicides," P.C. Kearney & D.D. Kaufman (eds), p. 293 (1969), Marcel Dekker, Inc., New York.
3. R.R. YEO, Weeds, 15, 42 (1967).
4. D.E. PACK, in "Analytical Methods for Pesticides, Plant Growth Regulators and Food Additives," Vol. V, G. Zweig (ed), p. 473 (1967), Academic Press, New York.
5. M. DAMANAKIS, Weed Res., 10, 77 (1970).
6. A.H. CORWIN, R.R. ARELLANO, A.B. CHIVVIS, Biochem. Biophys. Acta, 162, 533 (1968).
7. M. BEROZA and R.A. COAD, J. Gas Chromatog., 4, 199 (1966).
8. M.W. GOLDBERG and L.M. JAMPOLSKY, U.S. Patent 2,624,734 [C.A. 47, 12426c (1953)].
9. D.H. CORR and E.E. GLOVER, Chem. and Ind. 1964, 2128.
10. G. GROSSI and R. VECE, J. Gas Chromatog., 3, 170 (1965).
11. G.F. THOMPSON and K. SMITH, Anal. Chem., 37, 1591 (1965).